# Hadean greenstones from the Nuvvuagittuq fold belt and the origin of the Earth's early continental crust

# John Adam<sup>1</sup>, Tracy Rushmer<sup>\*1</sup>, Jonathan O'Neil<sup>2</sup>, and Don Francis<sup>3</sup>

<sup>1</sup>GEMOC, Earth and Planetary Sciences, Macquarie University, NSW 2109, Australia

<sup>2</sup>Department of Terrestrial Magmatism, Carnegie Institution of Washington, 5241 Broad Branch Road N.W., Washington, D.C. 20015, USA <sup>3</sup>Earth and Planetary Sciences Department, McGill University, 3450 University Street, Montreal, Quebec H3A 2A7, Canada

### ABSTRACT

To investigate formation of the Earth's earliest continental crust, partial-melting experiments were conducted (at 900-1100 °C and 0.5-3.0 GPa) on two greenstones from the 4.3 Ga Nuvvuagittuq complex of Quebec, Canada. For comparison, experiments were also conducted on a compositionally similar but modern arc volcanic (a Tongan boninite). At 1.5-3.0 GPa and 950-1100 °C, the experimentally produced melts are compositionally similar to the tonalite-trondhjemite-granodiorite (TTG) granitoids that compose most of Earth's early continental crust, including a 3.66 Ga tonalite that encloses the Nuvvuagittuq Complex. Because the degree of melting needed to produce the TTG-like melts is comparatively high (>30%), the relative concentrations of most incompatible elements in the melts are similar to those in their greenstone parent rocks. These greenstones have compositional affinities with modern subduction zone magmas and do not resemble mid-oceanic ridge basalts. That arc-like mafic rocks could have been selectively involved in TTG formation (in spite of their volumetrically subordinate status in most greenstone terrains) must reflect tectonic circumstances that were specific to their generation. These must have enabled accumulations sufficiently deep to melt at the 1.5-3.0 GPa needed to generate TTG magmas from eclogitic sources. They are also likely to have been related to some form of crustal recycling whereby mafic crust and water were returned to the mantle and arc-like mafic magmas generated as a consequence. To what degree these circumstances replicated modern plate tectonics is difficult to say, but it seems likely that, as in the modern Earth, the Hadean crust was organized into different tectonic environments and that one of these gave rise to the first continental crust.

#### INTRODUCTION

The Earth's oldest continental crust is composed primarily of granitic rocks known as tonalite-trondhjemite-granodiorite (TTG) (Jahn et al., 1981; Rudnick, 1995; Condie, 2005). These granites are classically associated with belts of metamorphosed volcanics and sediments known as greenstones. Although it is generally believed that TTG magmas were produced by partial melting of a basaltic crust that predated them (e.g., Drummond and Defant, 1990; Martin, 1994; Rapp et al., 2003; Condie, 2005), the tectonic environment in which this occurred is not known. Furthermore, whether there is a direct genetic relationship between TTGs and their immediate greenstone host rocks is also problematic (see Martin, 1987, 1994). These uncertainties have broader implications for studies of early Earth processes, including the question of when plate tectonics first became active. We have approached these issues by conducting partialmelting experiments on two greenstones from one of the oldest known greenstone belts, the Nuvvuagittuq complex of northern Quebec (see O'Neil et al., 2008, 2011). Our objective was to test for a direct genetic link between the Nuvvuagittuq greenstones and a closely associated but younger tonalite (PC-103) of the TTG series.

# EXPERIMENTAL STARTING MATERIALS AND BACKGROUND

The Nuvvuagittuq complex has been dated at 4.28 Ga using wholerock <sup>142</sup>Nd data (O'Neil et al., 2008). Although this Hadean age has been contested (Andreasen and Sharma, 2009), the greenstones have an independently established minimum age of 3.8 Ga (Cates and Mojzsis, 2007; David et al., 2008) and are undoubtedly among the oldest known terrestrial rocks. An enclosing but younger tonalite complex has been dated as 3.66 Ga (Cates and Mojzsis, 2007; David et al., 2008). This tonalite also has a <sup>143</sup>Nd depleted mantle model age of 4.2–4.4 Ga (O'Neil et al., 2008), consistent with a source of similar age to the 4.3 Ga Nuvvuagittug greenstones.

The Nuvvuagittuq greenstones include two stratigraphically and compositionally distinct groups (see O'Neil et al., 2011): these are (1) an incompatible element-depleted tholeiitic group, and (2) an overlying calc-alkaline group that is moderately enriched in incompatibles. The latter group includes a high-Ti and low-Ti series. Two samples (PC-227 and PC-162) (Fig. 1) from the second group were selected as starting materials for our experiments. These are among the most mafic and least altered of the Nuvvuagittuq greenstones collected by O'Neil et al. (2008, 2011). PC-162 belongs to the high-Ti series of O'Neil et al. (2011), whereas PC-227 belongs to the enriched low-Ti series. In spite of their age and current crystal assemblages (cummingtonite, chlorite, muscovite, zoisite, rutile, and plagioclase), both PC-162 and PC-227 have compositional similarities with modern low-Ca boninites (as defined by Crawford et al., 1989), although they are more aluminous and have less SiO<sub>2</sub>, Na<sub>2</sub>O, and Sr than typical Cenozoic boninites. The latter features were shown by Smithies et al. (2004) to be typical of Archean boninites relative to modern ones. Although not a unique occurrence (e.g., Kerrich et al., 1998; Polat et al., 2002), the resemblance of our samples to a type of modern arc volcanic is significant because the production of the latter is usually thought to depend on previous episodes of mantle melting and subsequent reenrichment via the recycling of older basaltic crust and hydrosphere into the mantle (see Cameron et al., 1983; Crawford et al., 1989). Because our greenstones may have undergone some chemical alteration during their history (explaining their relatively low concentrations of Sr and Na<sub>2</sub>O), we also conducted experiments on a fresh boninite glass (Station 25) dredged from the currently active North Tonga Trench



Figure 1. Incompatible element concentrations in Nuvvuagittuq greenstones PC-227 and PC-162, and average Cenozoic boninite (using data from Cameron et al., 1983). Data are normalized to primitive mantle (Sun and McDonough, 1989) concentrations.

© 2012 Geological Society of America. For permission to copy, contact Copyright Permissions, GSA, or editing@geosociety.org. *Geology*, April 2012; v. 40; no. 4; p. 363–366; doi:10.1130/G32623.1; 4 figures; 1 table; Data Repository item 2012099.

TABLE 1. ANALYSES OF STARTING MATERIALS, THE TONALITE PC-103 AND PARTIAL MELTS OF THE NUVVUAGITTUQ
GREENSTONES PC-227 AND PC-162, AND THE NORTH TONGAN BONINITE (STATION 25)

Sample or run	PC-227	PC-162	Station 25	PC-103	1961	1958	1973	R102	R91
Pressure (GPa)					3.0	2.0	1.5	2.0	1.5
Temperature (°C)					1100	1050	1050	950	1050
Starting material					PC-227	PC-227	PC-162	Station 25	Station 25
Percent melting					34	47	44	36	35
	green stone	green stone	boninite	tonalite	glass	glass	glass	glass	glass
SiO <sub>2</sub>	52.47	53.25	55.20	67.18	68.88	67.69	62.05	71.95	63.57
TiO <sub>2</sub>	0.40	0.47	0.45	0.46	0.71	0.47	0.60	0.46	0.63
Al,Ō,	17.19	15.96	11.00	16.18	13.43	15.72	17.38	14.16	15.93
FeO	9.44	10.24	7.85	3.80	3.57	3.38	5.37	2.42	5.03
MnO	0.21	0.22	0.17	0.08	0.06	0.03	0.08	0.03	0.09
MgO	11.13	9.48	13.08	2.24	3.46	2.42	3.23	1.40	3.55
CaO	7.45	8.43	9.73	3.69	6.10	5.65	7.45	3.59	6.58
Na <sub>2</sub> O	0.96	1.07	1.53	3.77	1.94	2.24	2.10	3.95	3.26
K,Ō	0.74	0.88	0.72	2.48	1.85	2.38	1.68	2.04	1.35
P,0,	0.01		0.26	0.12			0.06	0.28	0.28
Original total*	95.12	96.34	97.49	98.25	90.26	90.51	90.69	89.13	93.43
Mg no.	67.8	62.2	74.8	51.2	63.3	56.1	51.7	50.7	55.7

\*All analyses have been recalculated to 100%. Analysis of PG-103 is from O'Neil et al. (2008). PG-227 and PG-162 data are those of Rushmer and Adam. Station 25 boninite from Trevor Falloon. Mg no. = 100 × molecular Mg/(Mg + total Fe).

(Table 1). This is compositionally similar to our greenstone samples but has higher concentrations of Na<sub>2</sub>O and Sr.

# EXPERIMENTAL AND ANALYTICAL METHODS

Experiments were conducted on natural rock powders in an endloaded piston-cylinder apparatus. Run durations varied from 2 to 5 days. (For a full description of the experimental methods used, see Adam and Green, 1994.) The crystals and glasses (quenched melts) produced in experiments were analyzed for major, minor, and trace elements at the GEMOC Geochemical Analysis Unit (Department of Earth Sciences, Macquarie University, Australia). Major elements were analyzed by electron microprobe. Trace elements and some minor elements were analyzed in glasses by laser microprobe and inductively coupled plasma–mass spectrometry. Most crystals were either too small or inclusion rich to be reliably analyzed for trace elements, including standardizations, corrections, and uncertainties, see Adam and Green, 2006.) A full list of experiments, experimental conditions, run products, and run product analyses is provided in Tables DR1–DR3 in the GSA Data Repository<sup>1</sup>.

Although our experiments were not reversed, it is unlikely that they were significantly affected by disequilibrium. This is consistent with the compositional homogeneity of most of the experimentally produced glasses and crystals (see Table DR2). A second factor is the consistency of synthesized mineral compositions with both run conditions and published thermobarometers (Wood, 1974; Brey and Kohler, 1990; Nakamura, 2009) for coexisting mineral pairs. Calculated temperatures and pressures are generally within 100 °C and a few tenths of 1 GPa of actual run conditions, and close to the uncertainties of the thermobarometers used. Our experiments were conducted on relatively hydrous natural rock powders. The importance of this factor is difficult to quantify, but the main effects of high H<sub>2</sub>O concentrations would have been to lower liquidus temperatures and increase the relative stability of garnet against pyroxenes and (more particularly) plagioclase. Note that, although TTG magmas are usually assumed to have been hydrous (e.g., Drummond and Defant, 1990; Rapp et al., 2003; Condie, 2005), the actual H<sub>2</sub>O concentrations present in Archean TTG magmas are not known.

# RESULTS

At pressures of 0.5–2.0 GPa, orthopyroxene  $\pm$  olivine are the only near-liquidus phases of PC-227 (similar data were not collected for PC-162 and Station 25), consistent with similar results for Tertiary boninites (Umino and Kushiro, 1989; Van der Laan et al., 1989). However, under subliquidus conditions involving moderate to high degrees of melting (34%–47%), the melt phase has a broadly tonalitic-granodioritic composition (Table 1) and coexists with clinopyroxene  $\pm$  orthopyroxene  $\pm$  garnet  $\pm$  plagioclase. Major element concentrations vary with pressure, temperature, and source-rock composition (see Table DR2). They become increasingly SiO<sub>2</sub> rich with both increasing pressure and decreasing degree of melting (Fig. 2). At 1.5–3.0 GPa and 1100–1050 °C the partial melts of PC-227 are tonalitic, and at 2.0 GPa and 1050 °C are composi-



Figure 2. Compositions of experimentally produced glasses and natural tonalite-trondhjemite-granodiorite (TTG) plotted in quartz-plagioclase-olivine (Qtz-Plag-Ol) system. Major element concentrations in glasses and natural rocks have been converted to CMAS components (CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) using procedure of O'Hara (1968). TTG data are from Martin (1987). Straight lines through data points show approximate positions of cotectics for melts in equilibrium with garnet (or plagioclase) + clinopyroxene  $\pm$  orthopyroxene at 1.0, 1.5, 2.0, and 3.0 GPa (based on data from this study).

<sup>&</sup>lt;sup>1</sup>GSA Data Repository item 2012099, Tables DR1–DR3, is available online at www.geosociety.org/pubs/ft2012.htm, or on request from editing@geosociety .org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

tionally similar to the 3.66 Ga tonalite (PC-103) that encloses the Nuvvuagittuq complex, although they are noticeably less sodic and also more calcic (Table 1). Note that partial melts from similar experiments on the unaltered boninite (Station 25) have Na<sub>2</sub>O and CaO concentrations comparable to those in the natural tonalite (Table 1). The relative concentrations of most trace incompatible elements in the greenstone partial melts (Fig. 3) are also similar to those in PC-103 (Fig. 4), although their absolute concentrations are lower. They are relatively enriched in large ion lithophile elements (Rb, K, and Ba) and light rare earth elements (REE), but depleted in Nb, Ta, and heavy rare earth elements (HREEs).

### DISCUSSION AND CONCLUSIONS

The relatively low absolute concentrations of incompatible elements in the partial melts of PC-162 and PC-227 can be related to our choice of



Figure 3. Incompatible element concentrations in Nuvvuagittuq greenstone PC-227 and in tonalitic melts produced by partially melting PC-227 at 1.5 GPa and 1050 °C, and at 3.0 GPa and 1100 °C. Data are normalized to primitive mantle (Sun and McDonough, 1989) concentrations.



Figure 4. Incompatible element concentrations in average Nuvvuagittuq greenstone (O'Neil et al., 2008), tonalite PC-103 (O'Neil et al., 2008), and average tonalite-trondhjemite-granodiorite (TTG) composition (Martin, 1995). Natural TTGs and average Nuvvuagittuq greenstone replicate relationships produced by PC-227 and its tonalitic partial melts (Fig. 3). Normalization factors are same as used for Figures 1 and 3.

the most mafic greenstones as starting materials. On average, the Nuvvuagittug greenstones are considerably more enriched in incompatibles than our starting materials, although the relative concentrations of most elements are similar. If this factor is taken into account (cf. Figs. 3 and 4), it can be argued that PC-103 may have inherited most of its incompatible element characteristics from source rocks that already had similar features. Only the depletions in HREEs can be attributed to fractionation during melting as a result of their retention in residual garnet. Considering the similarity of PC-103 to other TTG granitoids (Fig. 3), this argument can be applied more generally. Thus in contrast to many previous proposals (e.g., Drummond and Defant, 1990; Foley et al., 2002), the distinctive compositional characteristics of TTGs (including low Nb, Ta, and Ti and high Rb, K, and Ba) may be the result of chemical fractionation that preceded TTG magma formation. This possibility is consistent with a number of other observations. One is that not all basalts can produce TTG-like melts. In fact, of the many experiments conducted on basaltic starting materials, very few have produced melts that genuinely resemble TTGs. This can partially be attributed to inappropriate experimental conditions, but it also reflects the compositional characteristics of the starting materials used in experiments (which are not always representative of Archean basaltic crust; see Rudnick, 1995). It has also been shown that the concentrations of most incompatible elements in Archean TTGs are too high for them to have been produced by the partial melting of the K-poor tholeiites that predominate in most greenstone terrains, but instead require crustal sources that were already enriched in these components (Smithies et al., 2009). The fact of enriched Hadean crust predating the earliest known continental crust has been independently verified by studies of Pb, Nd, and Hf isotopes in Paleoarchean rocks and zircons (Andreasen and Sharma, 2009; Blichert-Toft and Albarede, 2008; Tessalina et al., 2010). Taken together, these observations demonstrate that many of the compositional characteristics of the early continental crust must have been inherited from previous cycles of mantle depletion and subsequent reenrichment.

If TTGs were selectively derived from arc-like source rocks, it is highly likely that the latter were produced in a specific tectonic environment. This is because they must have been produced in large volumes (contrary to inferences based on of their volumetrically subordinate status in most greenstone terrains) and under circumstances that facilitated both their selective accumulation and subsequent partial melting. It is also probable that their production was linked to some form of crustal recycling whereby mafic crust and water were returned to the mantle and arc-like mafic magmas generated as a consequence. To what degree these circumstances would have resembled modern plate tectonics is difficult to say. However, there is sufficient evidence to suggest that, as in the modern Earth, the crust of the Hadean Earth was organized into a number of different tectonic environments and that one of these gave rise to the first continental crust. This is consistent with some form of horizontal tectonics and difficult to reconcile with models based purely on plume-driven tectonics.

# ACKNOWLEDGMENTS

This project was supported by Australian Research Council (ARC) grant DP0986232 to Rushmer. Norm Pearson and Peter Wieland assisted with the use of the electron microprobe and laser microprobe inductively coupled plasma–mass spectrometry facilities. We thank Trevor Falloon for providing the boninite sample (Station 25) from North Tonga, and David Champion and two anonymous reviewers for constructive reviews of the manuscript. This is publication 788 in the ARC National Key Centre for the Geochemical Evolution and Metallogeny of Continents (GEMOC). This study used instrumentation funded by ARC; the Linkage Infrastructure, Equipment and Facilities and the Department of Education, Licence and Training Systematic Infrastructure Grants, Macquarie University, and Industry.

## **REFERENCES CITED**

Adam, J., and Green, T.H., 1994, The effects of pressure and temperature on the partitioning of Ti, Sr and REE between amphibole, clinopyroxene and basaltic melts: Chemical Geology, v. 117, p. 219–233, doi:10.1016/0009-2541(94)90129-5.

- Adam, J., and Green, T.H., 2006, Trace element partitioning between mica- and amphibole-bearing garnet lherzolite and hydrous basanitic melt: 1. Experimental results and the investigation of controls on partitioning behaviour: Contributions to Mineralogy and Petrology, v. 152, p. 1–17, doi:10.1007/ s00410-006-0085-4.
- Andreasen, R., and Sharma, M., 2009, Neodymium-142 evidence for Hadean mafic crust: Comment: Science, v. 325, p. 267–269, doi:10.1126/science .1169604.
- Blichert-Toft, J., and Albarede, F., 2008, Hafnium isotopes in Jack Hills zircons and the formation of the Hadean crust: Earth and Planetary Science Letters, v. 265, p. 686–702, doi:10.1016/j.epsl.2007.10.054.
- Brey, G.P., and Kohler, T., 1990, Geothermobarometry in four-phase lherzolites II. New thermobarometers, and the practical assessment of existing thermobarometers: Journal of Petrology, v. 31, p. 1353–1378, doi:10.1093/petrology/ 31.6.1353.
- Cameron, W.E., McCulloch, M.T., and Walker, D.A., 1983, Boninite petrogenesis: Chemical and Sr-Nd isotopic constraints: Earth and Planetary Science Letters, v. 65, p. 75–89, doi:10.1016/0012-821X(83)90191-7.
- Cates, N.L., and Mojzsis, S.J., 2007, Pre-3750 Ma supracrustal rocks from the Nuvvuagittuq supracrustal belt, northern Quebec: Earth and Planetary Science Letters, v. 255, p. 9–21, doi:10.1016/j.epsl.2006.11.034.
- Condie, K.C., 2005, TTGs and adakites: Are they both slab melts?: Lithos, v. 80, p. 33–44, doi:10.1016/j.lithos.2003.11.001.
- Crawford, A.J., Falloon, T.J., and Green, D.H., 1989, Classification, petrogenesis and tectonic setting of boninites, *in* Crawford, A.J., ed., Boninites and related rocks: London, Unwyn Hyman, p. 1–49.
- David, J., Godin, L., Stevenson, R., O'Neil, J., and Francis, D., 2008, U-Pb ages (3.8–2.7 Ga) and Nd isotope data from the newly identified Eoarchean Nuvvuagittuq supracrustal belt, Superior Craton, Canada: Geological Society of America Bulletin, v. 121, p. 150–163, doi:10.1130/B26369.1.
- Drummond, M.S., and Defant, M.J., 1990, A model for trondhjemite-tonalitedacite genesis and crustal growth via slab melting: Archean to modern comparisons: Journal of Geophysical Research, v. 95, p. 21503–21521, doi:10.1029/JB095iB13p21503.
- Foley, S.F., Tiepolo, M., and Vannucci, R., 2002, Growth of early continental crust controlled by melting of amphibolite in subduction zones: Nature, v. 417, p. 837–840, doi:10.1038/nature00799.
- Jahn, B.-M., Glikson, A.Y., Peucat, J.J., and Hickman, A.H., 1981, REE geochemistry and isotopic data of Archaean silicic volcanics and granitoids from the Pilbara Block, Western Australia: Implications for the early crustal evolution: Geochimica et Cosmochimica Acta, v. 45, p. 1633–1652, doi:10.1016/S0016-7037(81)80002-6.
- Kerrich, R., Wyman, D., Fan, J., and Bleeker, W., 1998, Boninite series: Low Ti-tholeiite associations from the 2.7 Ga Abitibi greenstone belt: Earth and Planetary Science Letters, v. 164, p. 303–316, doi:10.1016/S0012-821X (98)00223-4.
- Martin, H., 1987, Petrogenesis of Archaean trondhjemites, tonalites and granodiorites from Eastern Finland: Major and trace element geochemistry: Journal of Petrology, v. 28, p. 921–953, doi:10.1093/petrology/28.5.921.
- Martin, H., 1994, The Archaean grey gneisses and the genesis of the continental crust, *in* Condie, K.C., ed., The Archaean crustal evolution: Amsterdam, Elsevier, p. 205–259.

- Nakamura, D.J., 2009, A new formulation of garnet-clinopyroxene geothermometer based on accumulation and statistical analysis of a large experimental data set: Metamorphic Geology, v. 27, p. 495–508, doi:10.1111/j.1525-1314 .2009.00828.x.
- O'Hara, M.J., 1968, The bearing of phase equilibria studies in synthetic and natural systems on the origin and evolution of basic and ultrabasic rocks: Earth-Science Reviews, v. 4, p. 69–133, doi:10.1016/0012-8252(68)90147-5.
- O'Neil, J., Carlson, R.W., Francis, D., and Stevenson, R.K., 2008, Neodymium-142 evidence for Hadean mafic crust: Science, v. 321, p. 1828–1831, doi:10.1126/science.1161925.
- O'Neil, J., Francis, D., and Carlson, R.W., 2011, Implications of the Nuvvuagittuq Greenstone Belt for the formation of Earth's early crust: Journal of Petrology, v. 52, p. 985–1009, doi: 10.1093/petrology/egr014.
- Polat, A., Hofmann, A.W., and Rosing, M.T., 2002, Boninite-like volcanic rocks in the 3.7–3.8 Ga Isua greenstone belt, West Greenland: Geochemical evidence for intra-oceanic subduction zone processes in the early Earth: Chemical Geology, v. 184, p. 231–254, doi:10.1016/S0009-2541(01)00363-1.
- Rapp, R.P., Shimizu, N., and Norman, M.D., 2003, Growth of early continental crust by partial melting of eclogite: Nature, v. 425, p. 605–609, doi:10.1038/ nature02031.
- Rudnick, R.L., 1995, Making continental crust: Nature, v. 378, p. 571–578, doi:10.1038/378571a0.
- Smithies, R., Champion, D., and Sun, S., 2004, The case for Archaean boninites: Contributions to Mineral Petrology: v. 147, p. 705–721.
- Smithies, R.H., Champion, D.C., and van Kranendonk, M.J., 2009, Formation of Paleoarchean continental crust through infracrustal melting of enriched basalt: Earth and Planetary Science Letters, v. 281, p. 298–306, doi:10.1016/j .epsl.2009.03.003.
- Sun, S.-s., and McDonough, W.F., 1989, Chemical and isotopic systematics of oceanic basalts, *in* Saunders, A.D., and Norry, M.J., eds., Magmatism in the ocean basins: Geological Society of London Special Publication 42, p. 313–345, doi:10.1144/GSL.SP.1989.042.01.19.
- Tessalina, S.G., Bourdon, B., Van Kranendonk, M., Birk, J., and Philippot, P., 2010, Influence of Hadean crust evident in basalts and cherts from the Pilbara Craton: Nature Geoscience, v. 3, p. 214–217, doi:10.1038/NGEO772.
- Umino, S., and Kushiro, I., 1989, Experimental studies of boninite petrogenesis, in Crawford, A.J., ed., Boninites and related rocks: London, Unwyn Hyman, p. 89–111.
- Van der Laan, S.R., Flower, M.J., and Koster van Groos, A.F., 1989, Experimental evidence for the origin of boninites; near-liquidus phase relations to 7.5 kb, *in* Crawford, A.J., ed., Boninites and related rocks: London, Unwyn Hyman, p. 112–147.
- Wood, B.J., 1974, The solubility of alumina in orthopyroxene coexisting with garnet: Contributions to Mineralogy and Petrology, v. 46, p. 1–15, doi:10.1007/ BF00377989.

Manuscript received 6 July 2011

Revised manuscript received 13 November 2011

Manuscript accepted 24 November 2011

Printed in USA